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(54) Title: FUEL FOR MOTOR VEHICLES

(57) Abstract: Fuel for motor vehicles comprising an emulsion between water and a liquid hydrocarbon, and an anti-cavitation additive comprising a copolymer including 20-80% in moles, preferably 35-70% in moles, of units containing at least one carboxylic group and 80-20% in moles, preferably 65-30% in moles, of units deriving from at least one monomer having an ethylene unsaturation, and wherein at least 20% in moles of the carboxylic groups, preferably 30-90% in moles, is in the form of at least one derivative selected from carboxylate salt, ester, amide and imide.

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FUEL FOR MOTOR VEHICLES

The present invention relates to a fuel for motor vehicles.

10 More specifically, the present invention relates to a fuel for motor vehicles which comprises an emulsion between water and a liquid hydrocarbon.

Even more specifically, the present invention relates to a fuel for diesel engines with a low emission of pollutants which comprises a high stability emulsion of water in
15 gas oil.

The new anti-pollution regulations which have come into force in Italy and the main European countries in the last few years, have compelled motor vehicle manufacturers
20 to significantly update internal combustion engines and fuel producers to offer fuels with a low environmental impact.

The introduction of so-called green gasoline and the use of catalytic converters have led to the necessity of
25 changing the feeding control system of Otto cycle engines,

which has passed from the carburetor method to the electronic injection method.

For similar reasons, in particular for reducing emissions of particulate and NOx, new Diesel cycle engines have been proposed, in which up-to-date electronic control systems have been introduced, which are capable of effecting the direct injection of fuel into the combustion chamber with pressures of over 1300 bar.

Furthermore, new ecological gas oils in emulsion form have been recently introduced onto the market, comprising an aqueous phase finely dispersed in the form of droplets in the hydrocarbon phase, stabilized by suitable emulsifying agents (see for example patent applications WO 97/34969, WO 00/15740 and WO 01/51593). The addition of controlled quantities of water to a fuel, in fact, significantly reduces the production of polluting agents. It is believed that this effect is the result of various phenomena activated by the presence of water in the combustion zones. Water, for example, by lowering the peak combustion temperature, reduces the emission of nitrogen oxides (NOx), whose formation is favoured by high temperatures. The instantaneous vaporization of water also favours a better dispersion of the hydrocarbon in the combustion chamber, thus greatly reducing the formation of particulate. These phenomena occur without jeopardizing the combustion process performance.

The use of injectors, both in gasoline and Diesel engines, and consequently very high feeding pressures, in particular for the latter, has created the necessity of developing and using new materials capable of sustaining, under typical internal combustion engine conditions, the stress imposed by new fuel feeding systems. In spite of this, the use of high pressures has led to erosion phenomena as a result of cavitation which can also be critical for the most advanced materials currently used in the transport industry. In particular, it has been verified that cavitation phenomena can arise in feeding devices as a result of brusque changes in the direction of the fluid on the feeding pipes of the pressurization pump or in the secondary pipes which lead to the injectors or on the tips of the injectors themselves.

Cavitation is the process which occurs when the pressure exerted on the fluid in a particular point is lower than the vapor pressure of the fluid itself (vaporous cavitation). In that point, the liquid vaporizes locally and forms cavities. These cavities, which can flow through the circuit carried by the fluid, subsequently come into contact with higher pressure regions and collapse. The resulting implosion can be extremely violent and can cause vibrations, noise and damage to the materials forming the circuit.

A phenomenon very similar to cavitation is generated by gases dissolved in the fluid (gaseous cavitation). If the pressure exerted on the liquid in a particular point is lower than the saturation pressure, the gas abandons the liquid forming bubbles. The bubbles initially increase in volume, but are then re-dissolved in the higher pressure areas of the circuit. Bubbles, however, may already be present in the fluid, for example, air dissolved in the fuel contained in a tank. As, in practice, it is extremely difficult to distinguish between these two cavitation processes, reference will be made herein, when speaking about cavitation, to both. Further details on cavitation can be found in SAE 982036 "Hydraulic system cavitation: A review" or in SAE 1999-01-2857 "Hydraulic system cavitation: part II - A Review of hardware design - related effect".

At present, attempts have been made to solve the problem of cavitation induced in fuels for motor vehicles, mechanically, as described, for example in U.S. patents 6,045,162 and 6,070,618.

The Applicants believe that the cavitation phenomena described above can become particularly significant with the use of fuels in the form of aqueous emulsion. These fuels, in fact, have a heterogeneous structure in which the conditions of the aqueous phase, that has a surface tension higher than that of the hydrocarbon, are more favourable

for forming cavities.

The Applicants consequently considered the problem of reducing the risk of activating erosion phenomena as a result of cavitation in internal combustion engines fed with
5 fuels in the form of aqueous emulsion, without jeopardizing the stability of the emulsion itself and without resorting to mechanical means.

The Applicants have found that the above problem can be solved by adding a polymeric additive containing carbox-
10 ylic groups and/or groups deriving from carboxylic groups as defined hereunder, to the fuel in the form of an aqueous emulsion.

An object of the present invention therefore relates to a fuel for motor vehicles comprising an emulsion between
15 water and a liquid hydrocarbon, and an anti-cavitation additive comprising a copolymer including 20-80% in moles, preferably 35-70% in moles, of units containing at least one carboxylic group and 80-20% in moles, preferably 65-30% in moles, of units deriving from at least one monomer hav-
20 ing an ethylene unsaturation, and wherein at least 20% in moles of the carboxylic groups, preferably 30-90% in moles, is in the form of at least one derivative selected from carboxylate salt, ester, amide and imide.

The copolymer according to the present invention pref-
25 erably has an average molecular weight Mw ranging from 700

to 3000.

The carboxylic groups can be partially or totally salified by means of a neutralization reaction carried out with an inorganic or organic base.

5 Examples of bases suitable for the reaction are hydroxides of alkaline or alkaline earth metals, ammonium hydroxide or quaternary ammonium hydroxides, sodium and/or potassium carbonates and bicarbonates, C₁-C₃₀ aliphatic alkylamines. The bases preferably used are sodium or ammonium
10 hydroxide.

Alternatively, the carboxylic groups can be partially or totally esterified using an alcohol or polyol with a low number of carbon atoms, selected, for example from: C₁-C₅ alcohols, such as methanol, ethanol, (iso)propanol,
15 (iso)butanol, ethylene glycol, glycerin and diethylene glycol.

The carboxylic groups can also be partially or totally transformed into amide or imide groups, by means of thermal treatment, with a primary or secondary aliphatic amine with
20 a low number of carbon atoms, selected, for example, from C₁-C₈ alkyl or dialkyl amines, such as ethyl amine, propyl amine, butyl amine, pentyl amine, hexyl amine, dimethyl amine, diethyl amine, dipropyl amine, dibutyl amine, etc.

Preferred monomers containing at least one carboxylic
25 group according to the present invention are:

(a) C₃-C₁₀ aliphatic monocarboxylic acids having an ethylene unsaturation, for example: acrylic acid, methacrylic acid, vinyl acetic acid, crotonic acid, allyl acetic acid, etc.

5 (b) C₄-C₁₀ aliphatic dicarboxylic acids having an ethylene unsaturation, for example: maleic acid, itaconic acid, citraconic acid, fumaric acid, methylene malonic acid, and the like, and their anhydrides.

Any monomers having an ethylene unsaturation capable
10 of copolymerizing with acids having an ethylene unsaturation, can be used in the preparation of the anti-cavitation agent according to the present invention. Typical examples include: C₂-C₁₂ α -olefins, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene, etc.; C₁-C₆ alkyl esters of
15 (meth)acrylic acid such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate; vinyl ethers and vinyl esters.

Examples of vinyl ethers are: vinyl methyl ether, vinyl ethyl ether, vinyl n-propyl ether, vinyl isopropyl
20 ether, vinyl n-butyl ether, vinyl isobutyl ether, vinyl t-butyl ether, vinyl hexyl ether.

Examples of vinyl esters are: vinyl formate, vinyl acetate, vinyl propionate, vinyl butyrate and vinyl pivalate.

25 A further object of the present invention relates to a

process for feeding an internal combustion engine, which comprises: feeding a fuel into a combustion chamber of said engine; igniting said fuel in said combustion chamber, wherein said fuel comprises an emulsion between water and a liquid hydrocarbon, and an anti-cavitation additive as described above. The preferred internal combustion engine is a diesel cycle engine.

The liquid hydrocarbon of the fuel for motor vehicles, object of the present invention, is generally a derivative from oil distillation and essentially consists of mixtures of aliphatic, naphthenic, olefinic and/or aromatic hydrocarbons. The liquid hydrocarbon preferably has a viscosity at 40°C ranging from 1 to 5.3 cSt and a density at 15°C ranging from 0.75 to 1.1 kg/dm³. Preferred liquid hydrocarbons according to the present invention are gas oils for diesel engines, kerosenes and aviation fuels.

The quantity of water present in the emulsion generally ranges from 2 to 40% by weight, preferably from 3 to 20% by weight, even more preferably from 4 to 10% by weight, with respect to the total weight of the emulsion. Any type of water can be used, both for industrial and domestic use. Demineralized or deionized water is preferably used, however, to avoid the formation of crusts on the internal surface of the combustion chamber or in the fuel flow areas, for example on the injectors.

The type of emulsion which characterizes the fuel for motor vehicles, object of the present invention, is generally of the water-in-oil type, in which the particles of water are dispersed in the continuous hydrocarbon phase.

5 In order to obtain emulsions which are stable over a period of time and with temperature variations, the use of at least one emulsifying agent is preferred, whose concentration depends on the quantity of water to be emulsified and the type of hydrocarbon used. Said concentration gener-
10 ally ranges from 0.1 to 10% by weight with respect to the total, preferably from 0.5 to 5%.

The emulsifying agent, or combination of emulsifying agents, preferably has an HLB (Hydrophilic-Lipophilic Balance) value ranging from 2 to 10, preferably from 3 to 8.

15 Emulsifying agents suitable for the purpose can be selected, for example, from:

(a) products obtained by the reaction of (a1) a polyolefinic oligomer functionalized with at least one group deriving from a dicarboxylic acid, or one of its de-
20 rivatives, with (a2) a polyoxy-alkylene comprising linear oxy-alkylene units, said polyoxy-alkylene being bound to a long-chain alkyl group optionally containing at least one ethylene unsaturation;

(b) products obtained by the reaction of (b1) a car-
25 boxylic acylating agent containing a hydrocarbon chain hav-

ing from 50 to 500 carbon atoms, with (b2) ammonia or an amine.

Emulsifying agents suitable for the purpose can also be selected from: alkanol amides, alkylaryl sulfonates, amino oxides, polyoxy-alkylenes (including ethylene oxide-propylene oxide block copolymers), ethoxylated or propoxylated/ethoxylated alcohols, carboxylates of ethoxylated or propoxylated/ethoxylated alcohols, ethoxylated or propoxylated/ethoxylated alkyl phenols, ethoxylated or propoxylated/ethoxylated amines and amides, ethoxylated or propoxylated/ethoxylated fatty acids, esters of fatty acids, ethoxylated or propoxylated/ethoxylated esters of fatty acids, esters of polyalcohols (preferably of ethylene glycol or glycerol), imidazoline derivatives, lecithins and derivatives, lignins and derivatives, mono-glycerides and derivatives, alkyl sulfonates, esters of phosphoric acid and derivatives, sorbitan derivatives, esters of sucrose and derivatives, or their mixtures.

Further details on emulsifying agents which can be used in the fuels according to the present invention are described in EP-A-475,620, EP-A-630,398, WO 97/34969, EP-A-812,615, WO 92/19701, WO 93/07238, WO 00/15740, whose contents are incorporated herein as reference.

A particularly preferred emulsifying agent is selected from the products of group (a) listed above.

The polyolefinic oligomer preferably has an average molecular weight ranging from 300 to 10,000, more preferably from 500 to 5,000, and is obtained by the homopolymerization or copolymerization of one or more olefins having
5 from 2 to 16 carbon atoms. The preferred polyolefinic oligomer is that containing at least 80% in moles of units deriving from isobutene, the remaining percentage consisting of units deriving from linear butene.

The polyoxy-alkylene comprises oxyalkylene units, each
10 containing two or three carbon atoms. The polyoxy-alkylene is preferably polyoxy-ethylene containing from 2 to 40, preferably from 5 to 20, oxy-ethylene units having the formula $-\text{CH}_2\text{CH}_2\text{O}-$.

The long-chain alkyl group bound to the polyoxy-
15 alkylene preferably derives from a C_8 - C_{24} fatty acid or fatty alcohol, optionally containing one or more ethylene unsaturations. Examples of fatty acids are: stearic acid, palmitic acid, myristic acid, lauric acid, oleic acid, etc. Examples of fatty alcohols are: octyl alcohol, decyl alcohol,
20 hol, lauryl alcohol, myristic alcohol, cetyl alcohol, oleic alcohol, etc.

More precise details on said emulsifying agent are provided in international patent application WO 01/51593, whose contents are incorporated herein as reference.

25 The emulsion thus obtained has a high stability over a

period of time, generally for over three months, without forming continuous aqueous phases inside the storage tank which can produce stratifications inside the hydrocarbon phase. This stability remains substantially unvaried also
5 with temperature conditions ranging from -20 to 50°C.

The stability of the emulsion, moreover, is not substantially jeopardized by the anti-cavitation agent. The latter is soluble in the emulsion and is present in concentrations ranging from 30 ppm to 3% by weight, preferably
10 from 50 ppm to 1.5% by weight, with respect to the overall weight of the emulsion.

The fuel for motor vehicles, object of the present invention, can contain other additives selected from: cetane number enhancers, corrosion inhibitors, lubricants, biocides, antifoam agents and anti-freeze agents. The cetane
15 number enhancers, for example, are products which tend to improve the detonating power of the fuel and are generally selected from nitrates, nitrites and peroxides of an organic or inorganic nature, soluble in aqueous phase or,
20 preferably, in the hydrocarbon phase. Organic nitrates, such as alkyl nitrates or cyclo-alkyls containing from 1 to 10 carbon atoms, are particularly preferred.

The biocides are selected from products known in the art, having this function such as, for example, derivatives
25 of morpholine, derivatives of isothiazolin-3-one,

tris(hydroxymethyl)-nitro methane, formaldehyde and their mixtures.

Finally, the fuel, object of the present invention, preferably also contains at least one anti-freeze additive to prevent the solidification of the water particles suspended in the hydrocarbon phase, when the environmental temperature drops well below zero. Examples of anti-freeze additives are alcohols such as methanol, ethanol, isopropanol and glycols such as ethylene glycol. The anti-freeze additive is generally added in a quantity ranging from 0.5 to 8% by weight, with respect to the total, preferably from 1 to 4%.

The fuel for motor vehicles, object of the present invention, can be prepared by mixing the components in dynamic emulsifying devices, through which the formation of the emulsion is effected by means of a mechanical action exerted by mobile parts, or by means of static devices, through which the emulsion components are passed at a high velocity or, alternatively, by means of a combination of the two types of devices. The emulsion can be formed by feeding the aqueous phase and hydrocarbon phase, optionally premixed, to the dynamic and/or static devices. The additives can be pre-dissolved in the two phases or added separately, together with the water and hydrocarbon phase.

CLAIMS

1. A fuel for motor vehicles comprising an emulsion between water and a liquid hydrocarbon, and an anti-cavitation additive, including a copolymer comprising
5 20-80% in moles of units containing at least one carboxylic group and 80-20% in moles of units deriving from at least one monomer having an ethylene unsaturation, and wherein at least 20% in moles of the carboxylic groups is in the form of at least one derivative
10 selected from carboxylate salt, ester, amide and imide.
2. The fuel for motor vehicles according to claim 1, wherein the copolymer has an average molecular weight Mw ranging from 700 to 3000.
- 15 3. The fuel for motor vehicles according to claim 1 or 2, wherein the carboxylic groups present in the copolymer are partially or totally salified by means of a neutralization reaction carried out with an inorganic or organic base.
- 20 4. The fuel for motor vehicles according to claim 3, wherein the base is selected from: hydroxides of alkaline or alkaline earth metals, ammonium hydroxide or quaternary ammonium hydroxides, sodium and/or potassium carbonates and bicarbonates, C₁-C₃₀ aliphatic al-
25 kyl amines.

5. The fuel for motor vehicles according to claim 1 or 2, wherein the carboxylic groups present in the copolymer are partially or totally esterified by means of an alcohol or a polyol with a low number of carbon atoms.
- 5 6. The fuel for motor vehicles according to claim 1 or 2, wherein the carboxylic acid groups present in the copolymer are partially or totally transformed into amide or imide groups by means of thermal treatment in the presence of a primary or secondary aliphatic amine
- 10 with a low number of carbon atoms.
7. The fuel for motor vehicles according to any of the previous claims, wherein the units containing at least one carboxylic group derive from a C₃-C₁₀ aliphatic monocarboxylic acid having an ethylene unsaturation,
- 15 or from a C₄-C₁₀ aliphatic dicarboxylic acid having an ethylene unsaturation.
8. The fuel for motor vehicles according to any of the previous claims, wherein the monomer having an ethylene unsaturation is selected from: C₂-C₁₂ α -olefins,
- 20 C₁-C₆ alkyl esters of (meth)acrylic acid, vinyl ethers and vinyl esters.
9. The fuel for motor vehicles according to any of the previous claims, wherein the liquid hydrocarbon has a viscosity at 40°C ranging from 1 to 5.3 cSt and a density at 15°C ranging from 0.75 to 1.1 kg/dm³.
- 25

10. The fuel for motor vehicles according to any of the previous claims, wherein the water is present in a quantity ranging from 2 to 40% by weight, with respect to the total.
- 5 11. The fuel for motor vehicles according to any of the previous claims, wherein the emulsion is of the water-in-oil type.
12. The fuel for motor vehicles according to claim 11, wherein the emulsion comprises at least one emulsifying
10 ing agent whose concentration ranges from 0.1 to 10% by weight with respect to the total.
13. The fuel for motor vehicles according to any of the previous claims, wherein said at least one emulsifying agent has an HLB (Hydrophilic-Lipophilic Balance)
15 value ranging from 2 to 10.
14. The fuel for motor vehicles according to claim 13, wherein said at least one emulsifying agent has an HLB (Hydrophilic-Lipophilic Balance) value ranging from 3 to 8.
- 20 15. The fuel for motor vehicles according to any of the previous claims, wherein said at least one emulsifying agent is a product obtained by the reaction of: (a1) a polyolefinic oligomer functionalized with at least one group deriving from a dicarboxylic acid, or one of its
25 derivatives; with (a2) a polyoxy-alkylene comprising

linear oxy-alkylene units, said polyoxy-alkylene being bound to a long-chain alkyl group optionally containing at least one ethylene unsaturation.

16. The fuel for motor vehicles according to any of the
5 claims from 1 to 14, wherein said at least one emulsifying agent is a product obtained by the reaction of (b1) a carboxylic acylating agent containing a hydrocarbon chain having from 50 to 500 carbon atoms, with (b2) ammonia or an amine.

10 17. A process for feeding an internal combustion engine which comprises: feeding a fuel to a combustion chamber of said engine; igniting said fuel in said combustion chamber, wherein said fuel comprises an emulsion between water and a liquid hydrocarbon, and an anti-cavitation additive according to any of the claims
15 from 1 to 16.

18. The process according to claim 17, wherein the internal combustion engine is a diesel cycle engine.

INTERNATIONAL SEARCH REPORT

International Application No.

EP2004/003037

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10L1/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/116868 A1 (MULLAY JOHN J ET AL) 29 August 2002 (2002-08-29) page 7, paragraph 118; claims page 8, paragraph 125 - paragraph 133	1-18
X	US 2001/034308 A1 (KRULL MATTHIAS ET AL) 25 October 2001 (2001-10-25) page 1, paragraph 18 - page 2, paragraph 21 page 3, paragraph 53 - paragraph 55 page 4, paragraph 63 page 8, paragraph 113 - paragraph 124	1-158
A	GB 1 075 254 A (BRITISH PETROLEUM CO) 12 July 1967 (1967-07-12) page 1, line 11 - line 18 ----- -/-	1-18

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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INTERNATIONAL SEARCH REPORT

International Application No.

EP2004/003037

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>TSUJINO ET AL.: "Effects of various polymer additives on cavitation damage" SAE TECHNICAL PAPER NR. 864969, 1 January 1986 (1986-01-01), XP008023446 I Mech E, UK the whole document</p> <p>-----</p>	1-18

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

EP2004/003037

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